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Differential Pulse Polarography of Phenylarsine Oxide

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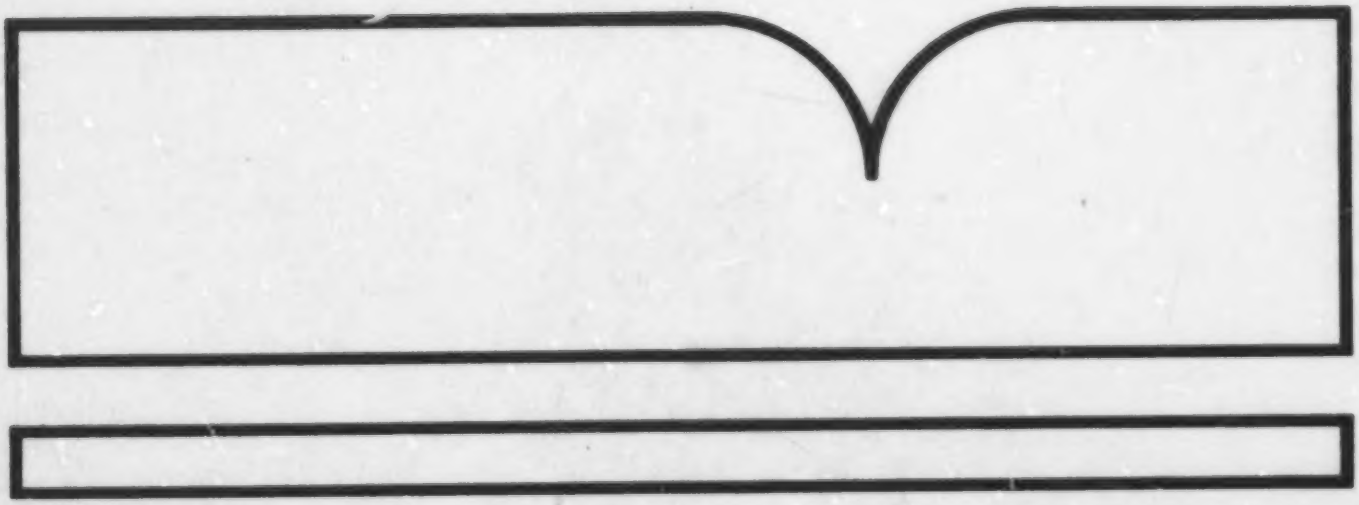

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Differential pulse polarography was applied to analyze for phenylarsine oxide (PAO) in aqueous solutions at different pH values. Optimization of the instrumental artifacts resulted in a detection limit of 10^{-8} M PAO at pH 7.3, a relative standard deviation of 1.7%, and a maximum sensitivity of 450 μA/mM PAO. The polarographic reduction of phenylarsine oxide was found to be pH dependent. Cyclic voltammetry and coulometry were used to characterize the electrode process.

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Differential Pulse Polarography of Phenylarsine Oxide

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Differential pulse polarography was applied to analyze for phenylarsine oxide (PAO) in aqueous solutions at different pH values. Optimization of the instrumental artifacts resulted in a detection limit of 10^{-8} M PAO at pH 7.3, a relative standard deviation of 1.7%, and a maximum sensitivity of 450 μA/mM PAO. The polarographic reduction of phenylarsine oxide was found to be pH dependent. Cyclic voltammetry and coulometry were used to characterize the electrode process.

Several studies have been reported on the polarographic reduction of organic arsenic species (*1–5*). This interest is the result of the use of these compounds as herbicides (*6*) as well as the fact that organic arsenic compounds may be produced from inorganic arsenic by natural biological processes (*7*).

The determination of inorganic arsenic by differential pulse polarography (DPP) (*8*) and differential pulse anodic stripping voltammetry (*9*) has been reported previously. The polarographic reduction of dimethylarsinic acid and methylarsonic acid has also been reported (*3*). Bess et al. (*4*) studied the DPP of a series of alkylarsonic and dialkylarsinic acids below pH 2. They found the peak potentials were pH dependent, shifting to more anodic values at lower pH values. Recently, Bess et al. (*5*) reported on the DPP of aromatic arsonic and arsinic acids. They found peak potentials as well as peak currents were pH dependent below pH 2.

Phenyl arsonic acid and phenyl arsonous acid were studied extensively by Watson and Svehla (*1, 2*) using dc polarography at a DME. They suggested that phenylarsine oxide (PAO) existed in aqueous solution as phenyl arsonous acid and the diffusion current was pH independent. Unfortunately, above pH 2 their waves were poorly formed and exhibited broad maxima. No data were presented above this pH, and most of the work was carried out in 0.1 M HCl at concentrations below 1×10^{-4} M, where PAO showed two main reduction processes. The half-wave potentials were shown to be pH dependent as the reduction processes became increasingly irreversible with increasing pH. A reaction scheme for PAO in 0.1 M HCl was proposed, where the reduction product reacts with the electroactive species with the formation of an insoluble polymeric product. The first wave was attributed to the reduction of PAO to phenylarsine, where each mole of phenylarsine combines with an additional two moles of PAO to form the insoluble polymeric product. The second wave was due to an increase in the fraction of PAO molecules that undergoes reduction to phenylarsine and a decrease in the fraction of PAO molecules that reacts with the phenylarsine. At this wave there is a net increase in the average number of electrons consumed per molecule of PAO. Further information on the reaction schemes can be found in their original article.

PAO is used as a titrant for the direct and indirect determination of residual chlorine and ozone in water and wastewater (*10*). Preliminary investigations on the direct measurement of PAO by DPP indicate that this technique is a promising method for lowering the detection limits in the indirect measurement of these oxidants (*11*). Since the control of pH is a necessary consideration in free and combined chlorine analysis with PAO (*10, 12*) as well as the stability and measurement of ozone (*10, 13*), an investigation of the effect of pH on the DPP of PAO was mandatory.

In the following discussion we describe the DPP behavior of PAO and suitable conditions for analysis. For the purpose of analytical method development, the effect of pH on the reduction of PAO was investigated, and the reduction was shown to have strong pH dependence. This is in contrast to earlier findings by Watson and Svehla (*1, 2*), emphasizing the need for a better understanding of the reduction processes. In addition to investigating the reduction processes, we have optimized instrumental artifacts (*14*) for the DPP technique, resulting in a highly reproducible analysis of PAO whose sensitivity is pH dependent.

EXPERIMENTAL

Apparatus. A Princeton Applied Research, Inc. (PAR) Model 174 Polarographic Analyzer and a Model 174/50 drop timer were used. A PAR Model 175 Universal Voltage Programmer was used for cyclic voltammetry. Temperature studies were conducted using the PAR Model 9350 water jacketed cell with a Haake TP-42

Table I. Constant Ionic Strength Buffers, $\mu = 0.025$

pH	buffer composition
1–4.8	HCl-$HC_2H_3O_2$-KCl
4.8–5.2	$HC_2H_3O_2$-$NaOH$-KCl
6.3–7.6	Na_2HPO_4-KH_2PO_4
8.3–8.9	H_3BO_3-$Na_2B_4O_7$
10.5	$NaHCO_3$-Na_2CO_3
12	$NaOH$-HCl-KCl

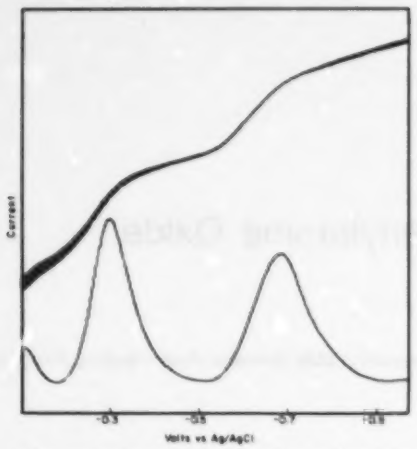


Figure 1. DC and DP polarograms of 2.57×10^{-5} M PAO at pH 1.8

constant temperature recirculating water bath. Coulometric experiments were performed with a PAR Model 379 coulometer and Model 377 cell system using a mercury pool electrode and 5 mL of electrolyte. Current was recorded on either a Houston Omnigraphic Model 200 X-Y recorder or a Honeywell Model 194 strip chart recorder.

A double Vycor junction Ag/AgCl reference electrode with a potential of −40 mV vs. SCE was used for all experiments. A platinum wire was used as the counter electrode. A Metrohm E-410 HMDE was used for cyclic voltammetry, and a DME with a natural drop time of 3 s at 49.5 cm with a flow of 3.05 mg/s was used for all polarograms unless otherwise stated.

Reagents. All chemicals were reagent grade and used without further purification. Triple distilled mercury was used throughout. All water was passed through mixed bed ion-exchange resins and triple glass distilled. Constant ionic strength buffers were prepared according to Perrin and Dempsey (*15*) and are given in Table I. Stock PAO solution (2.5×10^{-3} M) was prepared according to the standard method (*10*).

RESULTS AND DISCUSSION

As a preliminary examination, a dc polarogram of 2.5×10^{-5} M PAO at pH 1.8 was run and is shown in Figure 1. The DPP polarogram of the same solution is also given for comparison. Since Triton-X 100 and a high degree of damping were used to obtain the dc polarogram in Figure 1, Tast polarograms were run for the first reduction wave of 6.25×10^{-6} M PAO at pH values 1.8 and 8.7 ($\mu = 0.025$) to observe the effect of pH on the diffusion current and half-wave potential. The diffusion currents were 0.186 μA with an $E_{1/2}$ of −0.200 V and 0.06 μA with an $E_{1/2}$ of −0.756 V at pH 1.8 and 8.7, respectively.

Since our goal was the development of a sensitive technique for the analysis of PAO, further studies required the use of DPP. Using constant ionic strength buffers (*16*), 3.08×10^{-6} M PAO was examined throughout the pH range 1.8 to 12.5. In general, PAO exhibited three reduction peaks, A, B, and C, with varying pH dependencies, as shown in Figure 2. Two unresolved peaks, B and C, occurred at the more cathodic potential. At low pH, peak B predominates; while at high pH value, peak C predominates. At about pH 4.7, both peaks B

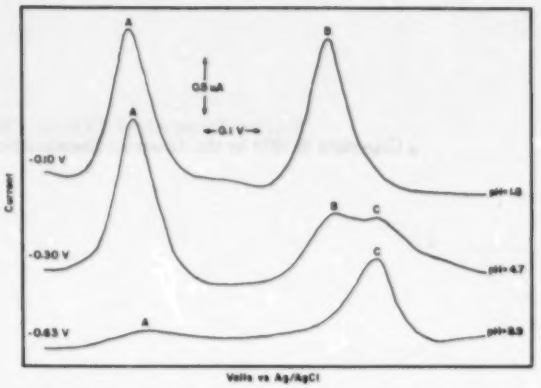


Figure 2. DPP of PAO at various pH values. [PAO] = 3.08×10^{-6} M; scan rate = 2mV/s; drop time = 2 s; pulse amplitude = 100 mV; ionic strength (μ) = 0.025

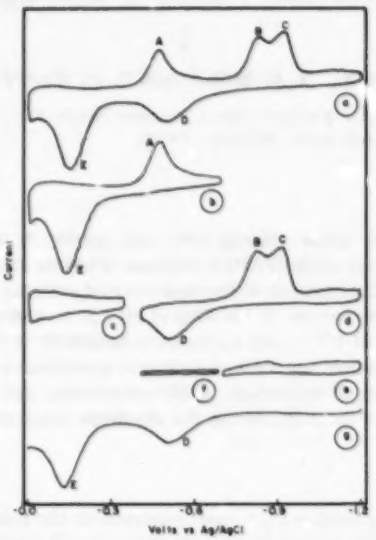


Figure 3. Cyclic voltammograms of PAO at an HMDE. [PAO] = 2.50×10^{-5} M; scan rate = 200 mV/s; HMDE area = 2.22 mm^2; $\mu = 0.025$; pH 4.7

and C approach equal height. Better resolution could not be obtained with decreases in scan rate (0.5 mV/s) or smaller modulation amplitudes (5, 10, 25 mV). The pH dependence of the current is inconsistent with the results reported by previous investigators (*1*, *2*). It is apparent that the pH dependence is not an artifact of DPP since Tast polarograms exhibit the same behavior. To determine if this behavior is characteristic of a DME only, an investigation of the mechanism of reduction of PAO by stationary electrode voltammetry and coulometry was initiated.

Voltammetry. The voltammetric behavior of PAO at an HMDE was investigated to aid in the resolution of the reduction processes. The experimental data reported below are uncorrected for spherical diffusion, charging current, or $1/\sqrt{t}$ decay of reduction current.

Cyclic voltammograms were obtained for 2.5×10^{-5} M PAO at a pH of 4.7 and are shown in Figure 3. It can be seen from this series of voltammograms that peak E represents the oxidation of the product of process A and peak D represents the oxidation of the product of process B and C.

In cyclic voltammetry, the mechanism of an electrode reaction can be studied by analyzing the variation of the experimental data with changes in the scan rate, concentration,

or pH. The peak current function, $i_p/C\sqrt{V}$ is a particularly useful diagnostic parameter in the evaluation of kinetic effects (*17*).

At a concentration of 1.18×10^{-5} M PAO and pH 4.7, the peak current function for A increased by 87% when the scan rate is increased from 0.1 V/s to 1.0 V/s while that for peak E decreased by 8%. On increasing the scan rate, peaks B and C formed a single peak (B) whose peak current function increased 23% over this scan range while that for peak D increased 134%. The peak potentials of peak A and peak B shifted cathodically 43 mV and 50 mV, respectively, over this scan range. The fact that cathodic shifts are observed together with the occurrence of anodic peaks implies that quasi-reversible electron transfers are involved in both reduction processes (*17*). On increasing the PAO concentration to 5.76×10^{-5} M from 1.18×10^{-5} M PAO at a scan rate of 0.2 V/s, the peak current function decreased 42% for A, 28% for B, 42% for C, and 23% for D. Very few processes other than adsorption cause the peak current function to both increase with increasing scan rate and decrease with increasing concentration (*18*).

A brief investigation, involving film stripping voltammetry, confirmed the presence of adsorption. At a given PAO concentration, adsorption and therefore i_p increased with increasing deposition time at a potential of −0.7 V for peak E and peak B in subsequent anodic and cathodic stripping voltammograms, respectively. No effect of the deposition time was observed on either peak A or B and C in cathodic stripping voltammograms after deposition at 0.0 V, or on peak D and E in anodic stripping voltammograms after deposition at −1.2 V (Figure 3E). This implies that the product of process A is adsorbed and is reduced in process B.

The diagnostic parameter, i_a/i_c, for product adsorption should approach unity at low scan rates (diffusion controlled) and increase at higher scan rates (adsorption controlled). For reactant adsorption the i_a/i_c ratio should approach unity at low scan rates and decrease at higher scan rates (*18*, *19*). It has already been shown that the product of peak A is adsorbed; however, the i_a/i_c ratio for peak E and A decreased from 3.1 at 0.1 V/s to 1.5 at 1.0 V/s. Where reactant adsorption has been shown (peak B), the i_a/i_c ratio for peaks D and B increased from 0.6 to 1.1. The deviation from the theoretical response could imply that another kinetic component such as a coupled chemical reaction could be involved. In cyclic voltammetric studies of phenylarsonic acid, Bess et al. (*5*) reported that both product and reactant adsorption could occur depending on the concentration examined. They also found that the reduction process was not entirely diffusion controlled and that coupled chemical kinetics did contribute to the total reduction current.

The occurrence of a pH dependent step involved in the reduction of PAO is apparent by examination of the peak current function with changing pH. The peak current function of A decreased 52% on increasing the pH from 1.2 to 7.6, while that for peak B decreased 20%. The E_p for peak A shifted cathodically 0.068 V/pH unit and peak B shifted cathodically 0.073 V/pH unit.

These results indicate that the reduction of PAO is probably the result of stepwise quasi-reversible electron transfers. The adsorption of the product of the first reduction process undergoes reduction at the second electron transfer and this process is further complicated by a pH dependent coupled chemical reaction.

Coulometry. Exhaustive microcoulometry was performed in 0.1 M $HClO_4$ and at a pH of 1.8 in the constant ionic strength buffer. This was done at the dc polarographic plateaus of each wave in order to determine the number of electrons involved in the reduction process. Electrolysis of 2.36×10^{-7} mol of PAO at either −0.35 V or −0.5 V at mercury pool cathode for the first wave was inconclusive because of unexplainable changes in the background current in the pH 1.8 buffer. In contrast, electrolysis at −0.35 V in 0.1 M $HClO_4$ gave very reproducible results, permitting calculation of the number of electrons. Eight replicate experiments of two different stock solutions performed over a two-day period gave an average n value of 2.02 with a standard deviation of 0.02. Electrolysis of three additions of 1.28×10^{-6} mol and four additions of 2.36×10^{-6} mol of PAO in 0.1 M $HClO_4$ resulted in an average n value of 2.01 with a standard deviation of 0.05. During these electrolyses, a precipitate was obtained and mass spectra analysis showed monomeric, dimeric, and trimeric mass units of (C_6H_5As) as well as evidence of higher mass units. No evidence corresponding to a mass unit of $(C_6H_5As)_3O$ or its fragmentation pattern was observed (*1*, *2*).

Electrolysis on the plateau of the second wave in the pH 1.8 buffer for seven replicate experiments for 2.36×10^{-7} mol of PAO resulted in a value for n of 3.92 ± 0.05. In 0.1 M $HClO_4$, electrolysis of 2.36×10^{-7} mol of PAO for seven experiments gave a value of 3.96 ± 0.08 for n. No precipitate was observed until the solution was allowed to stand exposed to air.

Electrolysis at −0.35 V in 0.1 M $HClO_4$ followed by electrolysis at −0.8 V for 2.36×10^{-7} mol of PAO resulted in 2 electrons per molecule at −0.35 V and another 1.6 electrons per molecule at −0.8 V. These results confirm the stepwise reduction mechanism indicated earlier by cyclic voltammetry. The fact that a total of only 3.6 electrons were found instead of 4 may be explained by adsorption of the insoluble product on the cell or electrodes, thereby preventing contact with the mercury. After electrolysis at −0.35 V, a differential pulse polarogram was scanned between +0.1 and −1.0 V and neither peak A or peak B was observed. The absence of peak B is due to the adsorption of the product of A on the mercury pool cathode.

A potential of +0.1 V was applied to the mercury pool, after electrolysis at −0.35 V, and a large anodic current flow was observed. A differential pulse polarogram was subsequently run and the reappearance of peak A and peak B was observed. This indicates that the product of the first electron transfer can be oxidized back to PAO and may represent the cyclic voltammetric peak E.

No DPP peaks were observed after electrolysis at −0.8 V followed by electrolysis at +0.1 V. Since cyclic voltammetry indicated that the second reduction is quasi-reversible, the product of that reduction must either be involved in irreversible chemical reaction or form a gas which is removed from solution by effusion.

Differential Pulse Polarography. *Effect of Temperature.* A common way of investigating the nature of the peak current of a reduction process is to observe the effect of temperature. Observing the change in peak currents with temperature can help to evaluate whether kinetic currents are involved. Diffusion controlled currents usually change by less than 2% per degree, while the effect on kinetic current may vary from 2 to 20% (*20*).

The change of i_p in the temperature range of 20–55 °C for all peaks as a function of pH are shown in Table II. These data indicate that most of the current is diffusion limited. Nevertheless, some kinetic current component is evident, which would be expected if a coupled chemical reaction is involved in the reduction mechanism. Increasing the temperature should decrease the peak height of adsorption controlled process; yet some adsorption processes can be diffusion controlled (*21*). Therefore, the temperature coefficients are not inconsistent with the adsorption observed by voltammetry.

Table II. Polarographic Characteristics of PAO

pH	peak A	peak B	peak C
	protons/electron		
1.8–3.8	1.1	1.1	...
4.7–6.8	1.8	...	2.00
	% $\Delta i_p/\Delta$°C		
1.8	+0.6	+4.2	...
7.6	−1.0	...	+4.0
8.9	+0.5	...	+1.1

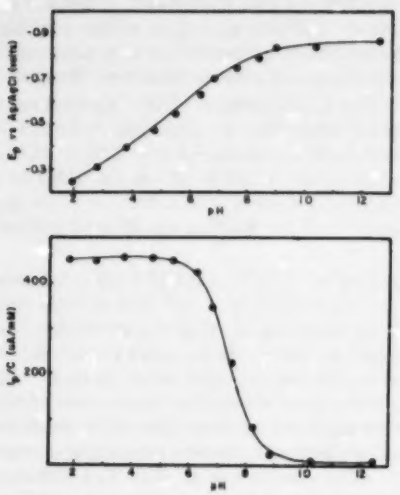


Figure 4. Dependence of peak current and peak potential for peak A on pH. [PAO] = 3.04 × 10^{-6} M; scan rate = 2 mV/s; drop time = 2 s; pulse amplitude = 100 mV; μ = 0.025

Effect of pH. PEAK A. The relationship between i_p and pH is shown in Figure 4 for peak A. The inflection point of this curve occurs at about pH 7.6. The plot of E_p vs. pH is also shown in Figure 4 and exhibits regions of pH dependence and independence. Linear regression analysis of the pH independent and dependent regions with solution of the appropriate equations results in a point of intersection at pH 7.6. The number of protons per electron (P/n) involved in the rate determining step can be determined from the slope of the line for the pH dependent region using the following equation:

$$E_p = \text{const} - \frac{RT}{F}\frac{P}{n}\text{pH}$$

The calculated values of P/n ratios are shown in Table II.

PEAKS B AND C. Figure 5 illustrates the dependency of i_p on pH for both peaks B and C. In the pH range 4 to 7, the measurement of peak currents and peak potentials was difficult due to the lack of peak resolution. The inflection point of the rising portion of the curve for peak C is approximately at pH 7.6. Above pH 10.3, no data were obtained because the peak coincided with the cathodic limit of the electrolyte.

The effect of pH on E_p for peaks B and C is also illustrated in Figure 5. Within the pH range where peak C could be distinguished from peak B (above pH 3.8), the effect of pH on E_p for C is the same as observed earlier for peak A. Using the same data analysis procedure, the lines of the pH independent and dependent regions were found to intersect at pH 7.6. The P/n ratios for B and C are given in Table II.

PEAK AREAS. The peak areas of A and the double peak, B plus C, measured with a planimeter, are expressed in

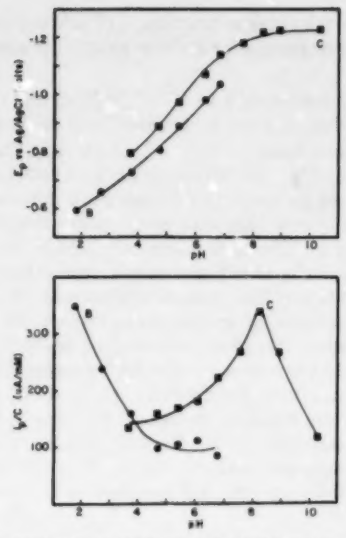


Figure 5. Dependence of peak currents and peak potentials on pH for peaks B and C. [PAO] = 3.08 × 10^{-6} M; scan rate = 2 mV/s; drop time = 2 s; pulse amplitude 100 mV; μ = 0.025

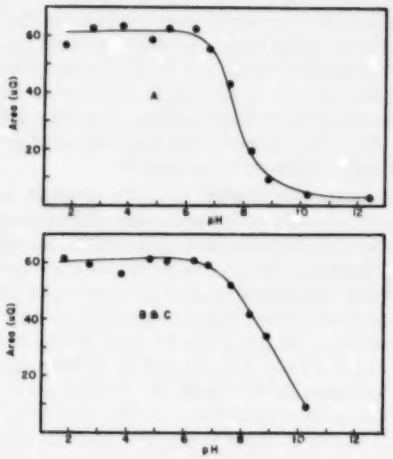


Figure 6. Peak areas as a function of pH. [PAO] = 3.08 × 10^{-6} M; scan rate = 2 mV/s; drop time = 2 s; pulse amplitude = 100 mV; μ = 0.025; μQ = microcoulombs

microcoulombs and illustrated in Figure 6 as a function of pH. The inflection point in the curve for peak A occurs at a similar pH to that reported above. These data correlate well with the pH dependence exhibited by the peak current functions of cyclic voltammetry. The DPP peak area of A decreased 52% over the pH range 1.2 to 7.6 while the cyclic peak current function of A decreased 52% over the same pH range. The area of B and C decreased 17% and the peak current function of B decreased 20%. This indicates that the mechanisms of reduction at an HMDE are similar to that of a DME.

In the pH independent range of 1.8 to 6.8, the ratio of the area of peak A to peak B plus C is 1.00 with a standard deviation of 0.007. In DPP, the increase in current at peaks B and C represents the difference in electron flow rate between that at A and that at B and C. Since the peak area ratio is 1.00, twice as many electrons flow at B and C than at A. This is consistent with the coulometric data of 2 electrons per molecule at A and 4 electrons per molecule at B and C.

Reversibility. For DPP, the peak half-width was shown to be dependent on both the amplitude of the applied pulse and the reversibility of the reduction process (22). The variation

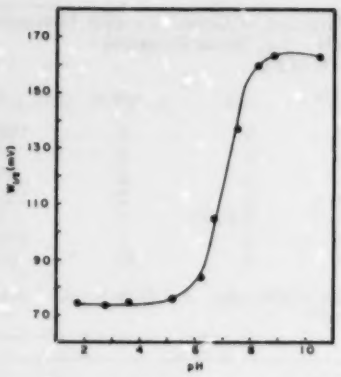


Figure 7. Dependence of peak half width ($W_{1/2}$) for peak A on pH. [PAO] = 3.08×10^{-6} M; scan rate = 2 mV/s; drop time = 2 s; pulse amplitude = 100 mV; μ = 0.025

in the reversibility of the reduction process for peak A vs. pH is shown in Figure 7. Smaller values of $W_{1/2}$ indicate a more reversible electrode process. Results shown in Figure 7 illustrate a change from reversible to irreversible conditions with increasing pH, and exhibit an inflection point at pH 7.6. These findings can be used to explain the shape of the i_p–pH curve for peak A (Figure 4). At low pH, high i_p values are indicative of a more reversible reduction; while at higher pH, the low i_p values are indicative of a less reversible reduction.

The change in the slope of the E_p–pH plots reflects this change of reversibility. At low pH, a $P/\alpha n_a$ of 1.1 would result in an α_a of 0.90 and at higher pH a $P/\alpha n_a$ of 1.8 would give α_a = 0.56. In DPP, using small values for the pulse amplitude (<25 mV) the peak half width ($W_{1/2}$) is given by the equation:

$$W_{1/2} = 3.52\frac{RT}{\alpha nF}$$

The value of α can be evaluated from this equation and a comparison can be made between the two reduction processes. The calculated values for A and B at pH 1.8 using this equation were 1.4 and 1.1, respectively. Using an n value of 2 for process B, since it represents a change in electron flow rate, the calculated value of α_A is 0.70 and α_B is 0.58. These α values indicate that A is more reversible than B.

The reversibility of the two electrode processes can be assessed by comparing the experimental and theoretical peak currents. For a reversible electrode reaction, the peak current is given by (*23*):

$$i_p = nFAC\sqrt{\frac{D}{\pi t}}\left(\frac{\sigma - 1}{\sigma + 1}\right)$$

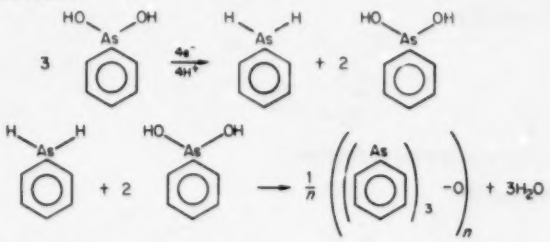
where t = the time after pulse application when the current is measured, $\sigma = \exp(-\Delta EnF/2RT)$, and ΔE = the pulse amplitude. Substituting n = 2 and assuming a diffusion coefficient of 1×10^{-5} cm^2/s (*21*), an i_p/C value of 46.2 μA/mM was calculated under the conditions employed (t = 48 ms, A = 2.89 mm^2, ΔE = 100 mV). The PAR 174 has a tenfold instrumental gain in the DPP mode. With this consideration, our experimental i_p/C values of 450 μA/mM for peak A and 362 μA/mM for peak B at pH 1.8 were actually 45.0 μA/mM and 36.2 μA/mM. Obviously peak A correlates more closely with the reversible theoretical current. It is of interest to note that ratio of the peak current of A to peak B is 1.2 and the ratio of α_A/α_B is 1.2, both indicating the same difference in reversibility.

Effect of Concentration. Since dc polarography can be used to determine concentrations of PAO as low as 5×10^{-5} M (*1*, *2*), it was decided to limit the major portion of this DPP investigation to concentrations lower than 2×10^{-5} M. Generally, at a pH of 1.8, both peaks A and B increased linearly over the concentration range 1.23×10^{-7} M to 1.23×10^{-5} M.

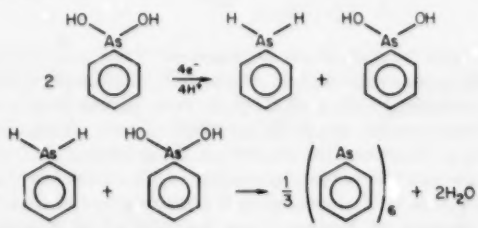
A brief investigation of higher concentrations resulted in the same behavior observed by the previous investigators (*1*, *2*). Increasing the PAO concentration to 2.36×10^{-4} M, the current function (i_p/C) for peak A decreased about 20% while that for peak B decreased 30%. It was also observed that a peak 0.08 V cathodic of peak B, assumed to be peak C, started to appear. At a concentration of 2.36×10^{-3} M, two peaks situated between peak A and B appeared and the current functioning for peaks A and B continued to decrease. Peak C was now predominant over peak B. Watson and Svehla (*1*, *2*) observed the inhibition of peaks A and B, the predominance of peak C, and determined that the two additional peaks were due to adsorption related to the first reduction process. They also found that the height of peak C was proportional to the concentration even after the inhibition of B.

Reduction Mechanisms. Watson and Svehla found 1.3 electrons per molecule for the first reduction process and 2 electrons per molecule for the second reduction process (*1*, *2*). They proposed the following mechanisms for the reduction of PAO in 0.1 M HCl based on the identification of the suspected products and intermediates:

Process I:



Process II:



It is evident that the coulometric and mass spectra findings in our paper are not consistent with these mechanisms.

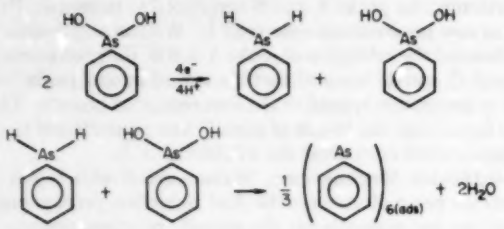
The discrepancy between the number of electrons per molecule found by Watson and Svehla (*1*, *2*) and our results possibly reflects the difference in the coulometric methods used. They performed a prolonged electrolysis of PAO and measured the subsequent decrease in wave height, while we based our interpretation on the exhaustive reduction of PAO. The products observed by Watson and Svehla probably represent intermediates formed in the bulk solution in the presence of PAO and not in the depleted zone at the electrode. These products can be further reduced during the exhaustive coulometry. Thus, the two mechanisms could represent initial and final states of the electroreduction of PAO.

We observed a pH dependence of the peak currents at a DME in contrast to the previous investigators (*1*, *2*). The reason for these differences is not clear. Our pH dependence has been shown not to be due to an artifact of DPP since Tast polarograms as well as cyclic voltammograms indicate a similar behavior. Perhaps the inconsistence can be partially explained by the fact that Watson and Svehla used solutions an order of magnitude more concentrated and the dc waves were poorly

formed and exhibited broad maxima above pH 2 (*1*, *2*). It is not unlikely that the reduction mechanisms may change with concentration or media composition. It may appear that the inflection at pH 7.6 observed frequently in our study represents an apparent pK for PAO. However, the pK value for PAO was reported to be 11 (*24*). Therefore, the pH dependence must represent changing reversibility and/or the effect of coupled kinetics.

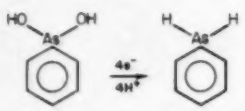
Based on our data as well as Watson and Svehla's mechanisms, a possible reaction path for the first wave is postulated:

Process I:



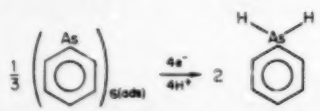
Watson and Svehla indicate that a 4-electron transfer would result in the formation of phenylarsine (gas). Therefore, based on our studies, the reaction path for the second wave would be as follows:

Process IIa:



or, for a stepwise reduction:

Process IIb:



In consideration of our proposed reduction mechanism, it would appear that the fact that peak A is inhibited at higher concentrations while peak C continues to increase proportional to concentration, would be inconsistent with a stepwise reduction. However, the adsorption of the product of Process I is the most probable explanation of the inhibition of peak A and peak B. Coulometry and voltammetry did show that the product of Process I can be reduced at Process II. Therefore, a probable explanation of this observed phenomenon would be that after the product of Process I undergoes reduction (Process IIb) the additional current flow could be due to the direct reduction of PAO (Process IIa).

Analytical Considerations. *DPP.* Since the current–concentration relationships below 2×10^{-5} M PAO are pH dependent, any analytical methodology involving the DPP of PAO will require strict pH control. The optimum sensitivity is obtained by using peak A in the lower pH range. The variation of the sensitivity with instrumental parameters was investigated over a PAO range of 1.23×10^{-6} M to 1.23×10^{-5} M. At a pH of 7.3 and a natural drop time of 3.4 s, the effect of pulse amplitude (MA), artificial drop time (τ), and scan rate (ν) on the sensitivity (i_p/C) are found in Table III. The greatest sensitivity for DPP is obtained with the largest drop, slowest scan rate, and the largest pulse amplitude (*14*). A calibration curve prepared using these conditions (See Table III) over the PAO range of 1.23×10^{-7} M to 1.54×10^{-6} M showed a sensitivity of 234 μA/mM with a relative standard deviation of 1.7% as determined from seven replicates of 1.54×10^{-6} M PAO. The limit of detection was determined by dividing three times the background current by the sensitivity

Table III. Variation of Sensitivity with Instrumental Parameters; pH = 7.3, Initial Potential = −0.350V, μ = 0.0025

MA, mV[a]	τ, s	ν, mV/s	i_p/C, μA/mM
100	2	2	190
50	2	2	78
25	2	2	33
100	1	2	129
100	0.5	2	77
100	2	5	148
100	2	10	99

[a] MA = pulse amplitude. τ = drop time. ν = scan rate. i_p/C = sensitivity.

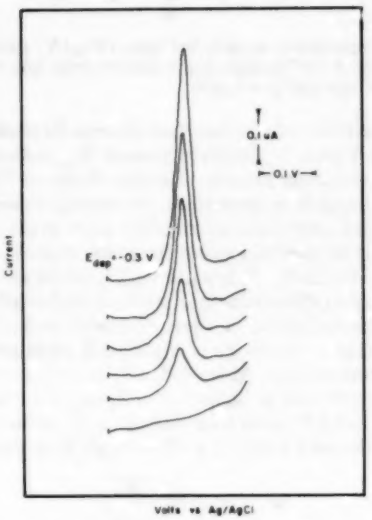


Figure 8. Differential pulse cathodic stripping voltammetry of PAO [PAO] = 2.36×10^{-8} M to 1.18×10^{-7} M; pH 1.2; HMDE area = 2.22 mm^2; τ_{dep} = 30 s; scan rate = 5 mV/s; pulse amplitude = 50 mV; pulse interval = 0.5 s

and was found to be 1.2×10^{-8} M PAO.

As mentioned earlier, this investigation was prompted by a desire to determine free chlorine in water. The standard titrimetric method (*10*) requires a pH range of 6.5 to 7.5 for the reaction of PAO with the free chlorine. This was the reason for choosing pH 7.3 for the above work. However, an even lower detection limit, approximately one-half that at pH 7.3, could be obtained in acidic media.

The analytical performance and versatility of this technique is being investigated by comparison with standard methods of analysis for oxidants in a variety of aqueous samples (*11*).

Stripping Voltammetry. The fact that the product of process A adsorbs and undergoes reduction at the second process at an HMDE suggested the possibility of determining lower levels of PAO by cathodic stripping voltammetry. A few experiments were conducted to investigate the analytical utility of this technique.

The production of the adsorbable species is controlled by the time that the potential at the HMDE is more cathodic than the first reduction process, yet more anodic than the second process. A differential pulse ramp was used because it often provides higher sensitivity using short deposition times. Utilizing a deposition time of 30 s at a potential of −0.3 V with an HMDE area of 2.22 mm^2 in a pH 1.2 buffer, the cathodic peak current was found to be proportional to the PAO concentration over the range 2.36×10^{-8} to 1.18×10^{-7} M PAO (Figure 8). Above this concentration range, the peak current became independent of the concentration. The sensitivity of the linear range was 3520 μA/mM. Seven

replicate determinations of 2.36×10^{-8} M PAO resulted in a relative standard deviation of 3.9%. Utilizing the method of Skogerboe and Grant (25) and the standard deviation of the 2.36×10^{-8} M PAO measurements, a detection limit of 2.3×10^{-9} M PAO was calculated.

The possibility of using the anodic peak E as well as coulometric stripping techniques is now under investigation for determining trace levels of PAO.

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